

into the corresponding aldehydes or ketones, the present method works well with diethyl secondary alkylphosphonates, yielding the corresponding ketones in good yields. However, in the case of a diethyl primary alkylphosphonate, conversion of an  $\alpha$ -hydroxyphosphonate into the aldehyde causes trouble due to the strongly basic condition and an aldol product was obtained as a byproduct.

### Experimental

A Typical Procedure for the Oxidation of Diethyl benzylphosphonate (Method A); To a stirred solution of diethyl benzylphosphonate (228 mg, 1 mmol) in tetrahydrofuran (4 ml) at  $-78^\circ\text{C}$  was added 0.7 ml of 1.5 M n-buthyllithium. After being stirred at  $-78^\circ\text{C}$  for 1 h, chlorodimethylborate (220  $\mu\text{l}$ , 2 mmol) was added to the reaction mixture at  $-20^\circ\text{C}$ . After 0.25 h at  $-20^\circ\text{C}$  and 1 h at room temperature, the solvent was evaporated in vacuo. The residue was dissolved in dichloromethane (4 ml) under nitrogen and added to a solution of m-chloroperoxybenzoic acid (258 mg, 1.5 mmol) in dichloromethane (4 ml) at  $-20^\circ\text{C}$ . After being stirred 1 h, the resulting solution was quenched with aqueous sodium bicarbonate (4 ml). The extractive workup and chromatographic separation gave diethyl  $\alpha$ -hydroxy benzylphosphonate (190 mg, 78%). Its spectral data were in accord with the reported data.<sup>9</sup> (Method B); The reaction mixture obtained by the MCPBA oxidation procedure outlined above was quenched with 50% aqueous sodium hydroxide solution (4 ml) and methanol (4 ml). The resulting solution was stirred for 50 min. The extractive workup and chromatographic separation gave benzaldehyde (66 mg, 62%).

### References

1. J. Boutagy and R. Thomas, *Chemical Review*, **74**, 87 (1974).
2. (a) H. J. Bestmann and O. Kratzer, *Chem. Ber.*, **96**, 1899 (1963); (b) S. S. Kulp and M. J. Mcgee, *J. Org. Chem.*, **48**, 4097 (1983).
3. (a) E. Vedejs, D. A. Enger, and J. E. Telschow, *J. Org. Chem.*, **43**, 188 (1978); (b) R. D. Little and S. O. Myong, *Tetrahedron Lett.*, **21**, 3339 (1980); (c) M. R. Galobardes and H. W. Pinnick, *Ibid.*, **22**, 5235 (1981).
4. J. R. Hwu, *J. Org. Chem.*, **48**, 4433 (1983).
5. D. S. Metteson, *Synthesis*, 147 (1974).
6. K. Fujita and M. Schlosser, *Helv. Chem. Acta.*, **65**, 1258 (1982).
7. J. B. Baudin, M. Julia, and C. Rolando, *Tetrahedron Lett.*, **26**, 2333 (1985).
8. Molecular oxygen gave inferior results for other substrates, as compared with chlorodimethylborate / MCPBA.
9. F. T. Boulet and A. Foucard, *J. Chem. Soc. Chem. Comm.*, 165 (1982).

### Synthesis and Structure of Bis[hydrotris(1-pyrazolyl)borato]iron(III) Nitrate

Sung-Hee Cho, Dongmok Whang, and Kimoon Kim\*

Department of Chemistry, Pohang Institute of Science and Technology, Pohang 790-600  
Chemistry Group, Research Institute of Industrial Science and Technology, Pohang 790-600

Received September 26, 1990

Tris(1-pyrazolyl)borate( $\text{HB}(\text{pz})_3^-$ ) ligand has been used in the syntheses of a variety of metal complexes.<sup>1</sup> The ligand is often considered as a cyclopentadienyl analogue as both ligands occupy effectively three coordination sites around a metal center and are both 6 electron donors. In recent years this ligand has received much attention in bioinorganic chemistry since the  $\text{N}_3$  ligand coordination mimics the multi-imidazole coordination found often in the active site of metalloenzymes.<sup>2,3</sup> One of the earlier types of complexes studied was the form  $\text{M}(\text{HB}(\text{pz})_3)_2$ , where M is a divalent metal ion. Crystal structures of two of these complexes,  $\text{Co}(\text{HB}(\text{pz})_3)_2^4$  and  $\text{Fe}(\text{HB}(\text{pz})_3)_2^5$ , have appeared. Although the structure of  $\text{Fe}(\text{HB}(\text{pz})_3)_2^+$  was mentioned ref. 3a,<sup>6</sup> the details of synthesis and crystal structure of the compound still remain unpublished. In an attempt to prepare new  $\mu$ -oxodiiron(III) complexes containing  $\text{HB}(\text{pz})_3^-$  ligands we accidentally obtained  $[\text{Fe}(\text{HB}(\text{pz})_3)_2](\text{NO}_3)^7$  as a major product. We report here the synthesis and X-ray structure of the compound.

### Experimental

All reagents were used as received.  $\text{KHB}(\text{pz})_3$  was synthesized by the literature methods.<sup>8</sup> UV-Vis and IR spectra were recorded on a Hewlett-Packard 8452A UV-Vis spectrophotometer and a Perkin Elmer 843 IR spectrophotometer, respectively. Elemental analysis was performed in the Korea Research Institute of Chemical Technology. Solid state magnetic susceptibilities were measured with a magnetic susceptibility balance (Johnson Matthey). Solution susceptibilities were determined by the NMR method<sup>9</sup> with a Bruker AM-300 MHz spectrometer.

**$[\text{Fe}(\text{HB}(\text{pz})_3)_2](\text{NO}_3)$ .** A solution of 0.126 g (0.50 mmol) of  $\text{KHB}(\text{pz})_3$  in 2 ml of  $\text{H}_2\text{O}$  was added dropwise to a clear orange brown solution containing 0.200 g (0.50 mmol) of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 0.042 g (0.50 mmol) of  $\text{NaHCO}_3$  and 5 ml of  $\text{H}_2\text{O}$  with vigorous stirring. A brown solid precipitated immediately; however, with stirring the suspension took on a deep red appearance. After 12 h the mixture was filtered and the solid was dried under vacuum to afford 0.117 g of a red solid (yield 70%). When the procedure was repeated with 0.075 g (0.18 mmol) of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 0.093 g (0.36 mmol) of  $\text{KHB}(\text{pz})_3$  without adding  $\text{NaHCO}_3$  to the solution the same product was obtained in higher yield (0.085 g, 85%). UV-Vis (MeCN):  $\lambda_{\text{max}}(\epsilon)$  242(sh, 9600), 272(sh, 3900), 442 (5200), 520(sh, 1400) nm. IR(KBr,  $\text{cm}^{-1}$ ): 3120, 3100, 2540 (BH), 1490, 1400, 1370, 1350, 1310, 1210, 1190, 1120, 1070, 1050, 990, 770, 710, 660, 620, 460, 330. Anal. Calcd for  $\text{C}_{18}\text{H}_{20}\text{N}_3\text{O}_3\text{B}_2\text{Fe} \cdot \text{H}_2\text{O}$ : C, 38.47; H, 3.95, N, 32.40. Found: C, 38.54; H, 3.56; N, 32.41.

**X-ray Crystal Structure Determination.** Dark red crystals of  $[\text{Fe}(\text{HB}(\text{pz})_3)_2](\text{NO}_3)$  suitable for an X-ray analysis were grown by slow diffusion of ether into a  $\text{CH}_2\text{Cl}_2$  solution of the compound. A crystal having approximate dimensions of

**Table 1.** Crystallographic Data for  $[\text{Fe}(\text{HB}(\text{pz})_3)_2](\text{NO}_3)$ 

formula	$\text{FeO}_3\text{N}_{13}\text{C}_{18}\text{B}_2\text{H}_{20}$
fw	543.91
space group	triclinic, $P\bar{1}$ (No. 2)
$a$ , Å	11.252(2)
$b$ , Å	12.018(1)
$c$ , Å	12.189(2)
$\alpha$ , deg	118.65(1)
$\beta$ , deg	96.34(1)
$\gamma$ , deg	113.94(1)
vol, Å <sup>3</sup>	1222.7
$Z$	2
temp, °C	23
$d(\text{calcd})$ , g/cm <sup>3</sup>	1.477
radiation	graphite monochromated Mo $K\alpha$ ( $\lambda(K\alpha_1)=0.7093$ Å)
linear abs. coeff., cm <sup>-1</sup>	6.6
scan mode	$\omega-2\theta$
scan width, deg	$0.70+0.34 \tan\theta$
$2\theta$ limits	$6 < 2\theta < 50$
data collected	4500
unique data	4060
unique data with $F_o^2 > 3\sigma(F_o^2)$	3136
No. of variables	337
$R$	0.056
$R_w$	0.063

$0.40 \times 0.25 \times 0.20$  mm was mounted on an Enraf-Nonius CAD 4 diffractometer using Mo  $K\alpha$  radiation. Cell parameters and an orientation matrix for data collection were obtained from least squares refinement, using the setting angles of 24 reflections in the range  $23.4^\circ < 2\theta < 30.8^\circ$ . The crystallographic data and additional details of data collection are summarized in Table 1. The intensities of 4 standard reflections, recorded every 3 h of X-ray exposure, showed no systematic changes. All the calculations were carried out with the Enraf-Nonius Structure Determination Package (SDP). The intensity data were corrected for Lorentz and polarization effects and empirical absorption corrections were also applied. The structure was solved by a combination of Patterson and difference Fourier methods. The centrosymmetric space group  $P\bar{1}$  was assumed and proved to be correct as the structure refined satisfactorily by full-matrix least squares methods. All the nonhydrogen atoms were refined anisotropically. The positions of hydrogen atoms were idealized and included in the calculations of the structure factors as fixed contributions. The final cycle of refinement led to the  $R$  indices listed in Table 1. The atomic scattering factors were taken from International Tables<sup>10</sup> for the nonhydrogen atoms and from literature<sup>11</sup> for hydrogen. The final positional and equivalent isotropic thermal parameters of the nonhydrogen atoms are listed in Table 2. Table S1<sup>12</sup> and S2<sup>12</sup> list the anisotropic thermal parameters and the final values of observed and calculated structure factors, respectively.

## Results and Discussion

At the outset of this work we hoped to obtain the  $\mu$ -oxo

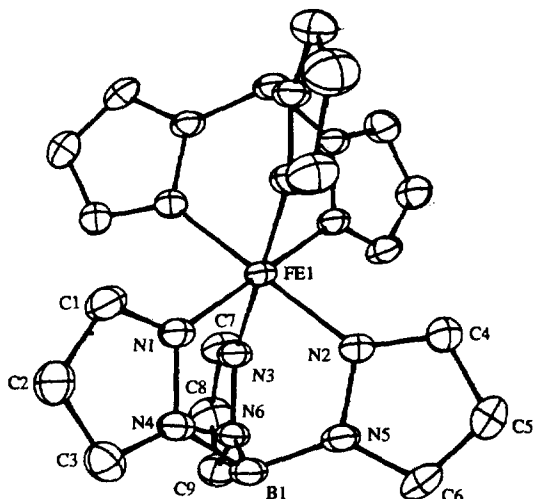
**Table 2.** Positional and Equivalent Isotropic Thermal Parameters for  $[\text{Fe}(\text{HB}(\text{pz})_3)_2](\text{NO}_3)$ 

Atom	x	y	z	$B_{eq}(\text{Å}^2)$
Fe1	0.000	0.000	0.000	2.39(2)
Fe2	0.500	0.000	0.500	2.23(2)
O1	0.5903(6)	0.3426(7)	0.1696(7)	10.2(3)
O2	0.7553(6)	0.4680(6)	0.3536(6)	10.5(2)
O3	0.7397(7)	0.5746(6)	0.2693(7)	12.2(3)
N1	-0.1125(4)	-0.0850(4)	0.0815(4)	2.8(1)
N2	0.1656(4)	0.1260(4)	0.1675(4)	2.9(1)
N3	-0.0424(4)	0.1574(4)	0.0742(4)	2.9(1)
N4	-0.1004(4)	0.0067(4)	0.2102(4)	2.8(1)
N5	0.1503(4)	0.1938(4)	0.2898(4)	2.8(1)
N6	-0.0328(4)	0.2275(4)	0.2053(4)	2.8(1)
N7	0.5171(4)	-0.0069(4)	0.3398(4)	2.8(1)
N8	0.5377(4)	0.2030(4)	0.5856(4)	2.6(1)
N9	0.7017(4)	0.0833(4)	0.5694(4)	2.6(1)
N10	0.6194(4)	0.1147(4)	0.3533(4)	2.8(1)
N11	0.6447(4)	0.3036(3)	0.5788(4)	2.7(1)
N12	0.7917(4)	0.1952(4)	0.5612(4)	2.6(1)
N13	0.6918(5)	0.4583(5)	0.2566(6)	5.6(2)
C1	-0.2073(5)	-0.2235(5)	0.0372(5)	3.3(1)
C2	-0.2580(6)	-0.2228(5)	0.1356(5)	3.9(2)
C3	-0.1880(6)	-0.0752(5)	0.2433(5)	3.6(1)
C4	0.2985(5)	0.1645(5)	0.1933(5)	3.1(1)
C5	0.3739(5)	0.2605(5)	0.3333(5)	3.5(1)
C6	0.2770(5)	0.2747(5)	0.3886(5)	3.2(1)
C7	-0.0791(6)	0.2209(5)	0.0246(5)	4.1(2)
C8	-0.0951(6)	0.3318(5)	0.1215(6)	4.7(2)
C9	-0.0646(5)	0.3319(5)	0.2346(5)	3.8(2)
C10	0.4406(6)	-0.1107(5)	0.2070(5)	3.5(2)
C11	0.4933(6)	-0.0556(6)	0.1349(5)	4.1(2)
C12	0.6050(6)	0.0874(5)	0.2307(5)	3.7(1)
C13	0.4799(5)	0.2741(5)	0.6572(5)	3.2(1)
C14	0.5489(6)	0.4209(5)	0.6991(6)	3.8(2)
C15	0.6532(5)	0.4353(5)	0.6475(5)	3.3(1)
C16	0.7813(5)	0.0579(5)	0.6313(5)	3.4(1)
C17	0.9207(6)	0.1495(6)	0.6631(5)	4.1(2)
C18	0.9232(5)	0.2344(5)	0.6165(5)	3.2(1)
B1	0.0085(6)	0.1764(6)	0.2895(5)	3.0(2)
B2	0.7284(6)	0.2526(5)	0.4980(5)	2.9(1)

$$*B_{eq} = 8/3\pi^2 \sum_i \sum_j U_{ij} a_i a_j \mathbf{a}_i \cdot \mathbf{a}_j$$

diiron complex,  $\text{LFeO}(\text{HCO}_3)_2\text{FeL}$  ( $\text{L}=\text{HB}(\text{pz})_3$ ) from the reaction of  $\text{Fe}(\text{NO}_3)_3$  with  $\text{HB}(\text{pz})_3^-$  in aqueous solution containing  $\text{NaHCO}_3$ . Instead, the reaction produced  $[\text{Fe}(\text{HB}(\text{pz})_3)_2](\text{NO}_3)$  as a major product, which could be obtained in high yield from  $\text{NaHCO}_3$  free solution by using a 2:1 ligand:metal ratio.

The crystal structure of  $[\text{Fe}(\text{HB}(\text{pz})_3)_2](\text{NO}_3)$  consists of the packing of two crystallographically independent  $\text{Fe}(\text{HB}(\text{pz})_3)_2$  cations occupying two different special positions and a nitrate anion residing on a general position. Both cations have inversion symmetry and only half portions of each are thus crystallographically unique. The structures of the two cations, one of which is shown in Figure 1, are almost identi-



**Figure 1.** Structure of one of the two cations (cation 1) in  $[\text{Fe}(\text{HB}(\text{pz})_3)_2](\text{NO}_3)$  (40% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

**Table 3.** Selected Bond Distances(Å) and Angles(°)

	Cation 1	Cation 2
Fe1-N1	1.958(5)	1.950(5)
Fe1-N2	1.959(3)	1.960(4)
Fe1-N3	1.952(5)	1.947(4)
N1-N4	1.366(5)	1.360(6)
N2-N5	1.386(6)	1.361(6)
N3-N6	1.368(6)	1.375(6)
N1-C1	1.330(6)	1.342(5)
N2-C4	1.321(7)	1.333(8)
N3-C7	1.33(1)	1.326(9)
N4-C3	1.336(8)	1.341(7)
N5-C6	1.341(6)	1.344(7)
N6-C9	1.339(9)	1.333(7)
N4-B1	1.554(6)	1.560(5)
N5-B1	1.523(9)	1.525(8)
N6-B1	1.54(1)	1.54(1)
N1-Fe1-N2	89.5(2)	89.1(2)
N1-Fe1-N3	89.0(2)	87.9(2)
N2-Fe1-N3	88.5(2)	88.9(2)
Fe1-N1-N4	119.8(3)	119.9(2)
Fe1-N2-N5	118.6(3)	119.9(3)
Fe1-N3-N6	119.8(4)	120.1(4)
Fe1-N1-C1	133.3(3)	133.0(4)
Fe1-N2-C4	133.4(3)	133.6(4)
Fe1-N3-C7	133.6(4)	133.4(4)
N4-B1-N5	106.9(5)	106.5(4)
N4-B1-N6	106.4(4)	106.5(4)
N5-B1-N6	107.1(5)	106.7(5)

cal. Selected bond distances and angles are given in Table 3. The coordination geometry around Fe(III) ion is close to a regular octahedron: Fe-N distances range 1.947(4) to 1.960(4) Å and N-Fe-N angles 87.9(2) to 89.5(2)°. The average Fe-N distance(1.954(5) Å) and average N-Fe-N angle(88.8(5)) agree with those for  $\text{Fe}(\text{HB}(\text{pz})_3)_2^+$  reported in ref. 3 within

experimental errors. The average Fe-N distance is considerably shorter than those in high spin Fe(III) complexes,  $[\text{Fe}_2\text{O}(\text{O}_2\text{CCH}_3)_2(\text{HB}(\text{pz})_3)_2]$  (2.160 Å)<sup>3</sup> and  $[\text{Et}_4\text{N}][\text{Fe}(\text{HB}(\text{pz})_3)\text{Cl}_3]$  (2.16 Å)<sup>13</sup>, and somewhat shorter than those in low spin Fe(III)-N<sub>6</sub> complexes,  $\text{Fe}(\text{phen})_3(\text{ClO}_4)_3$  (1.973 Å)<sup>14</sup> and  $[\text{Fe}(\text{[9]aneN}_3)_2]\text{Cl}_3 \cdot 5\text{H}_2\text{O}$  (1.99 Å)<sup>15</sup>. The short Fe-N distances indicate that  $[\text{Fe}(\text{HB}(\text{pz})_3)_2](\text{NO}_3)$  is a low spin complex. This has been confirmed by the magnetic susceptibility measurements both in solution(2.67 BM) and in solid state(2.15 BM). Pyrazole rings of  $\text{HB}(\text{pz})_3$  ligand in the complex are almost planar and other structural parameters of the ligand,  $\langle\text{B-N}\rangle$  (1.54(1) Å),  $\langle\text{N-N}\rangle$ (1.37(1) Å),  $\langle\text{N-C}\rangle$  (1.33(1) Å), and  $\langle\text{C-C}\rangle$  (1.38(1) Å), are not different from their typical values in its transition metal complexes.<sup>3-5,13</sup>

**Acknowledgement.** We gratefully acknowledge financial support from Research Institute of Industrial Science and Technology. We also thank Dr. Y. K. Shim of Korea Research Institute of Chemical Technology for the help in obtaining elemental analysis results.

## References

- (a) S. Trofimenko, *Prog. Inorg. Chem.*, **34**, 115 (1986); (b) A. Shaver, "Comprehensive Inorganic Chemistry", G. Wilkinson, R. D. Gillard and J. A. MacClevarty, Eds., Oxford, England, Vol. 2, 245 (1987).
- J. S. Thompson, T. J. Marks and J. A. Ibers, *J. Am. Chem. Soc.*, **101**, 4180 (1979).
- (a) W. H. Armstrong, A. Spool, G. C. Papaefthymiou, R. B. Frankel and S. J. Lippard, *J. Am. Chem. Soc.*, **106**, 3653 (1984); (b) W. H. Armstrong and S. J. Lippard, *ibid.*, **106**, 4632 (1984); (c) W. H. Armstrong and S. J. Lippard, *ibid.*, **107**, 3730 (1985).
- M. R. Churchill, K. Gold and C. E. Maw, Jr., *Inorg. Chem.*, **9**, 1957 (1970).
- J. D. Oliver, D. F. Mullica, B. B. Hutchinson and W. O. Milligan, *Inorg. Chem.*, **19**, 165 (1980).
- It is not clear what was used for the counter anion of  $[\text{Fe}(\text{HB}(\text{pz})_3)_2]^+$  in their crystallographic study.
- The first  $[\text{Fe}(\text{HB}(\text{pz})_3)_2]^+$  appeared in the literature was prepared by oxidation of  $\text{Fe}(\text{HB}(\text{pz})_3)_2$  with  $\text{I}_2$  and isolated as a  $\text{PF}_6^-$  salt. However, the details of synthesis and characterization were not reported. P. R. Sharp and A. J. Bard, *Inorg. Chem.*, **22**, 2689 (1983).
- (a) S. Trofimenko, *Inorg. Synth.*, **12**, 99 (1970); (b) S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 3170 (1967).
- D. F. Evans, *J. Chem., Soc.*, 2003 (1958).
- "International Tables for X-ray Crystallography", Vol. IV, Kynoch, Birmingham, England (1974).
- R. F. Stewart, E. R. Davison and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- Supplementary materials. These are available from the corresponding author upon request.
- (a) H. Fukui, M. Ito, Y. Moro-oka and N. Kitajima, *Inorg. Chem.*, **29**, 2868 (1990); (b) S. -H. Cho, D. Whang, S. K. Chung and K. Kim, Abstracts of the 65th Korean Chemical Society Meeting, 90 (1990)
- J. Baker, L. M. Engelhardt, B. N. Figgis and A. H. White, *J. C. S. Dalton Trans.*, 530 (1975)
- J. C. A. Boeyens, A. G. S. Forbes, R. D. Hancock and K. Wieghardt, *Inorg. Chem.*, **24**, 2926 (1985).